

SUBCONTRACT TITLE: **ADVANCED PROCESSING OF CdTe- AND $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ -
BASED SOLAR CELLS**

SUBCONTRACT NO: **NDJ-2-30630-18**

REPORT FOR: Phase III/Quarter 1

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This is the progress report for the 1st quarter (01/04 – 03/04) of Phase III for above subcontract. The project deals with two thin film technologies: CdTe and CIGS. The focus areas include: (a) CdTe – stability, novel back/front contacts, and the development of manufacturing friendly processes; (b) CIGS – development of two-step non-co-evaporation technology.

Part I – CdTe

Front Contact:

In this report we include data on a series of devices fabricated on all-sputtered front contacts based on ITO and In_2O_3 , with the latter serving as the resistive “buffer” layer.

Indium tin oxide (ITO) is the second (after SnO_2) most widely used front contact material for CdTe solar cells. Although in many cases it has been found to be very effective, it has also been shown to form “non-ohmic” front contacts [1]. This was interpreted as a “surface effect”, as the work function of ITO has been found to vary from 4.0 to 5.0 eV, depending on the concentration of O_2 at the surface of the film [2]. Figure 1 shows the light J-V characteristics for CdTe cells fabricated on ITO/ In_2O_3 bi-layers; for this set of devices the objective was to study the effect of the buffer (In_2O_3) thickness. The J-V characteristic around V_{OC} , of the cell fabricated directly on ITO (i.e. In_2O_3 thickness 0 Å), suggests that the front contact (i.e. ITO/CdS) is rectifying and seems to support the findings of others [1,2]. The inclusion of the high-p In_2O_3 (thickness 25-200 nm) results in devices with essentially identical characteristics; the main variations among these cells are in series resistance, but these are small and do not correlate with the thickness of In_2O_3 . In order to further evaluate the effectiveness of In_2O_3 as a buffer layer, a series of cells with varying CdS and In_2O_3 thicknesses were fabricated; V_{OC} 's and FF's are summarized in Fig. 2. In general, the thickness of In_2O_3 seems to have a rather minor effect on performance (with one exception); however, as the thickness of the CdS is decreased performance degrades consistently, clearly demonstrating the key problem when thin CdS films are utilized for the fabrication of CdTe solar cells. Nevertheless, In_2O_3 appears to be an effective buffer layer, and for this case (used with ITO), it is also beneficial in improving the contact with CdS, eliminating the rectifying behavior obtained for cells fabricated directly on ITO; this is presumably due to a change in the O_2 concentration on the ITO surface.

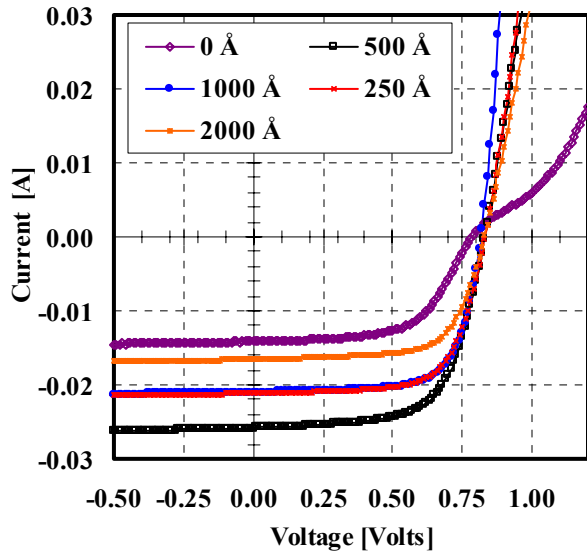


Figure 1. Light J-V characteristics of ITO/In₂O₃/CdS/CdTe cells.

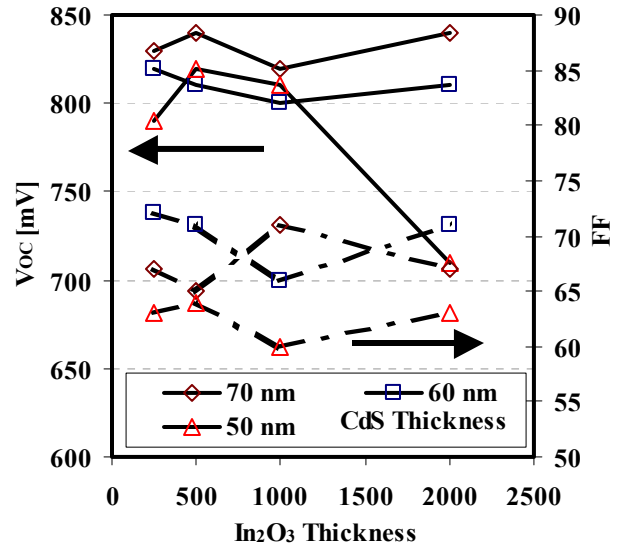


Figure 2. The effect of In₂O₃ and CdS thicknesses on V_{oc} and FF.

Collection Losses and the Apparent Diode A-Factor

During a previous team meeting we presented monochromatic light J-V measurements (similar results were included in last years report[3]) that suggested that the FF in CdTe cells, even in state-of-the-art devices, is limited by collection losses. Figure 3 shows monochromatic light J-V data; the measurements are taken using interference filters with a bandwidth of 20 nm, and the light intensity is adjusted to match within 10% the corresponding AM1.5 equivalent at each wavelength. It is clear from the data in Fig. 3 that short wavelength J-V (i.e. for strongly absorbed light) have high FF's, while at longer wavelengths, the J-V begins to exhibit a "softer knee", and therefore lower FF's. The dependence of the FF on wavelength is shown in Fig. 4 for two devices; the dotted lines mark the white light (AM1.5) FF. It is believed that the lower FF for long wavelengths is due to the fact that a significant fraction of deeply generated carriers are not collected at forward bias. It should be noted that one of the devices has a white light FF of approx. 71% and a "blue FF" of 75%. These results clearly suggest that the FF of CdTe devices is collection limited.

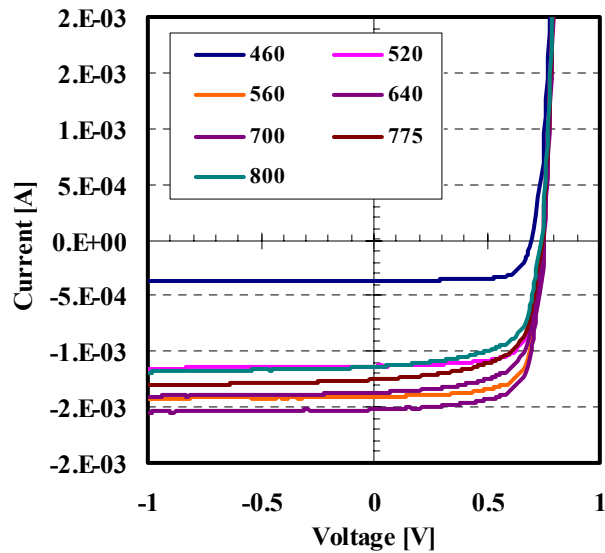


Figure 3. Monochromatic light J-V for a typical CdTe device.

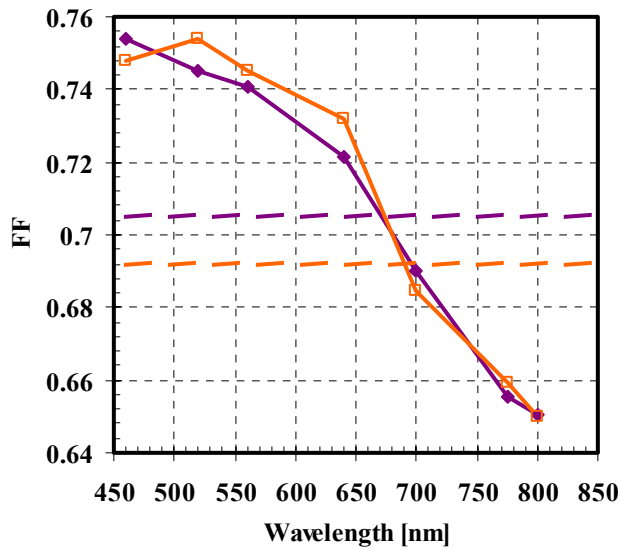


Figure 4. The dependence of the FF on wavelength; dotted lines mark the corresponding white light FF.

Collection losses can also have a significant effect on the calculation of the “light A-factor”, a quantity often used to characterize devices and interpret their performance characteristics. The assumption of a constant J_L and superposition, can lead to overestimations of the light A-factor. Figure 5 shows the calculated collection function ($H(V)$) vs. voltage for typical cells; the calculations/estimates are based on the assumption that collection is 100% for strongly absorbed light (i.e. 520 nm). The calculations were limited to 0.6 Volts because at higher voltages the assumptions are no longer valid. Table I lists device data calculated for three cases: (a) for a constant J_L , (i.e. $H(V)=1$), and for the calculated collection functions (b) at 640 and (c) at 700 nm (as shown in Fig. 5). The light A-factors were calculated at V_{OC} (i.e. @ .85 V). It is clear that even when using the two lowest collection functions shown in Fig. 5, the effect of collection losses on “A”, the FF and the total power loss is significant.

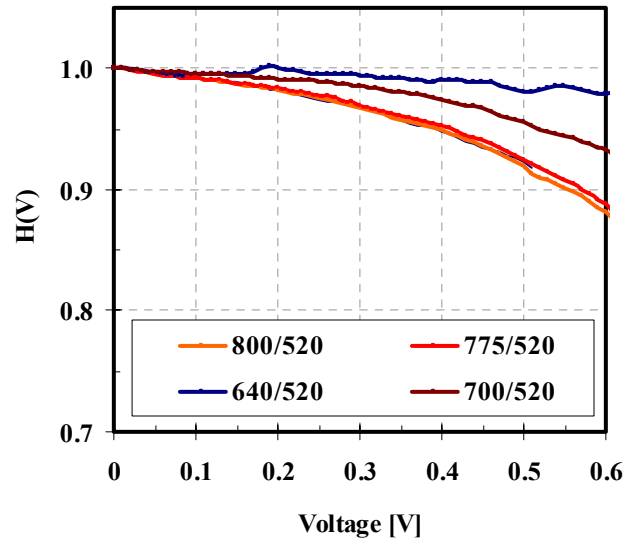


Figure 5. Calculated collection functions for various wavelengths, assuming 100% collection for strongly absorbed light (i.e. 520 nm)

Table I. The effect of $H(V)$ on the light A-factor, the FF, and power loss for a typical CdTe device; calculations are based on the collection functions at 640 and 700 nm shown in Fig. 5.

	$H(V)=1.0$	$H(640)$	$H(700)$
J_o [A]	1.00E-11		
A (light)	1.60	1.76	2.10
J_L [A]	0.025		
V_{OC} [mV]	850	1.76	
FF	83.3%	80.5%	72.5%
FF Loss		3.4%	13.0%
Pwr Loss		3.5%	14.90%

Zn₂SnO₄ Buffer Layers

The study of Zn₂SnO₄ (ZTO) as a buffer layer has continued. Previous work has indicated that cell performance is very sensitive to various fabrication parameters when ZTO is used as the buffer; these include the Zn/Sn ratio, the annealing temperature, the film thickness and the CdCl₂ heat treatment temperature. As-deposited films lead to poor solar cell characteristics, and annealing at 600°C has been found to yield optimum performance[3]. In this report the effect of ZTO thickness on solar cell performance is summarized in Figs 6 and 7. The ZTO films were deposited with a Zn/Sn ratio of 2.0, and were heat treated at 600°C. Their thickness was varied as indicated in the figures below (500, 750, 1250Å). The two sets of devices shown in

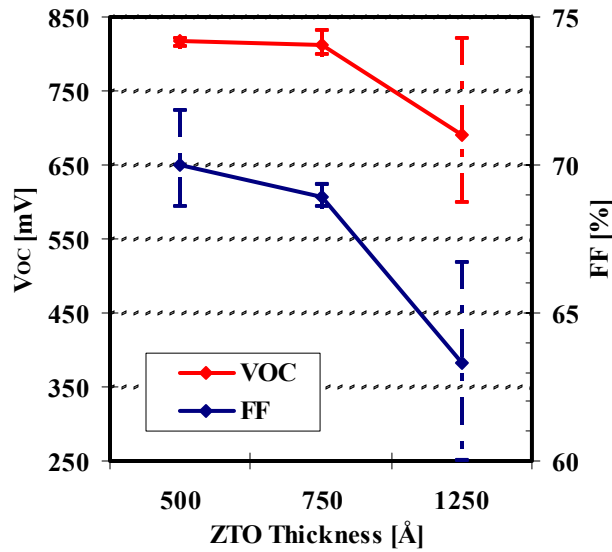


Figure 6. V_{OC} and FF for $\text{SnO}_2/\text{ZTO}/\text{CdS}/\text{CdTe}$ cells CdCl_2 heat-treated at 390°C .

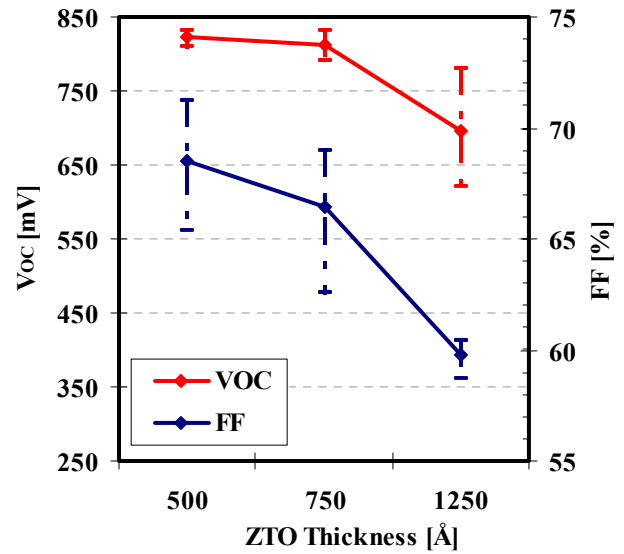


Figure 7. V_{OC} and FF for $\text{SnO}_2/\text{ZTO}/\text{CdS}/\text{CdTe}$ cells CdCl_2 heat-treated at 400°C .

Figs 6 and 7 were CdCl_2 heat-treated at 390 and 400°C respectively. From these data it is apparent that the thickness of ZTO is critical to solar cell performance, with smaller thicknesses leading to improved V_{OC} 's and FF's. The CdCl_2 heat treatment temperature is not as critical in this case; however, the scatter in the data appears to increase at 400°C . Differences in the SR of these devices are not consistent at this time and further work is necessary to identify additional factors that may be influencing the device characteristics.

Part II - CIGS

Substrate Effects – Glass Cleaning

We have been reporting on the effect of substrate preparation conditions on device performance. In particular we have addressed the role of Na and Mo in influencing device performance. Both clearly play a role in a complex interplay of defects and impurities. While Na is an impurity, it is necessary to help balance compensation. The Mo deposition conditions can modulate Na access, but also influence defect formation due to structural influences on growth. The upshot is that everything matters. This is not surprising in that every time we introduce a new batch of glass we expect some affect on performance. In many cases the negative effect is so large that we simply throw the glass away and secure a new batch. At an industrial level we could set quality control standards for our supplier and reduce such fluctuations. At an R&D level we tolerate these reality factors and use them to enrich our understanding.

Clearly two additional factors that require understanding and control are the glass itself and the glass cleaning procedure. We expect that with improved understanding of the role of all impurities in glass on performance we could adjust the cleaning procedure to contain the fluctuations of the impurities in the glass. As discussed above, the progress that we have made on this thus far is with Na. What we have learned about controlling Na may also be controlling other impurities as well, but we have no data yet to support that possibility. In working through these issues with Na we found it necessary to change our glass cleaning procedure to accommodate environmental concerns related to our primary solvent. We have been using trichloro,trifluoro-ethane as a degreasing agent because of the consistent high level performance that it produced. However, it was placed on the list of solvents that endangered the ozone layer, so we decided to replace it. This proved to be a non-trivial exercise, since glass cleaning is more art than science, and coupling that with a sensitive device added to the difficulty.

Our cleaning process consists of a soap and water scrub followed by a thorough water rinse. The next step is the one we focus on here, an ultrasonic solvent soak again followed by a thorough rinse in de-ionized water. As the substrates are removed from the rinse tank they are carefully blown dry with nitrogen.

In our search for a new solvent we kept all of the other cleaning steps constant

as well as the CIGS deposition process. Routine device performance for trichloro,trifluoro-ethane was Voc's in the 450 mV range, FF's in the .65 range and Jsc's in the 38 mA/cm² range. Because we knew that trichloro,trifluoro-ethane had special properties our first thought was to continue its use but at a much reduced level. This was tried by doing the first and longest ultrasonic soak in trichloro-ethane and following with a brief soak in

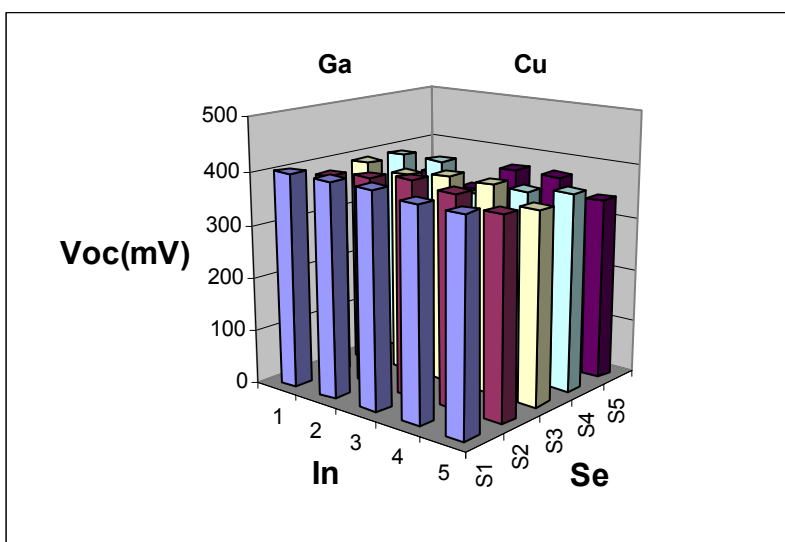


Figure 1. Voc profile of 25 CIGS devices resulting from use of trichloro-ethane/trichloro,trifluoro-ethane as the glass cleaning agent.

trichloro,trifluoro-ethane. The results for the Voc profile are shown in figure 1. What is shown is our usual profile of 25 0.1 cm² devices and the positions of the elemental sources relative to that profile. As can be seen, while the uniformity is reasonably good, the Voc's are down by about 50 mV. Also, a closer look reveals a possible dependence on the Cu/In ratio in that the Voc's seem to drop systematically from the In to the Cu side. This suggests an interplay between Cu and Na. There is discussion of this in the literature, and we also have interpreted some of the results from our experiments with Mo in these terms[4]. Here it is tempting to speculate that trichloro,trifluoro-ethane is more effective at removing Na than trichloro-ethane, and that the films from this procedure have excess Na.

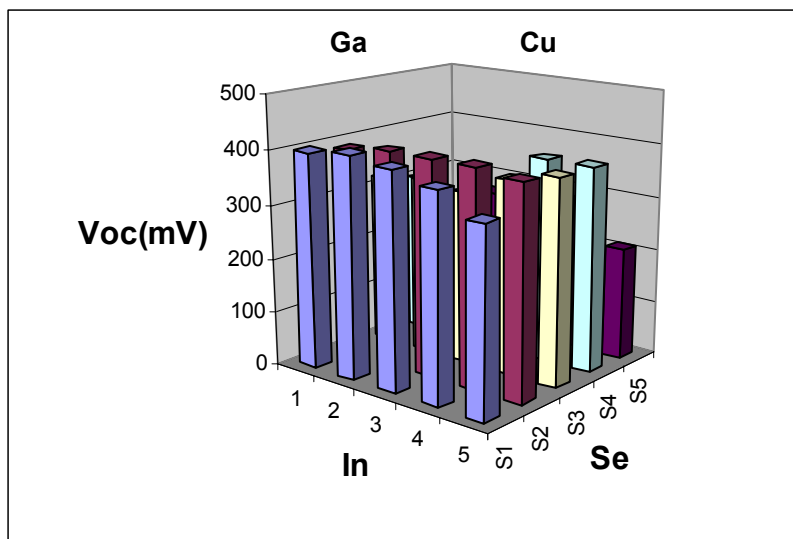


Figure 2 Voc profile of 25 CIGS devices resulting from use of methanol/trichloro-ethane as the glass cleaning agent.

While we may be able to further improve the Voc's with this procedure by reducing the Cu level, it is not clear that this would be a viable solution. In particular we might expect the devices to be unstable if we are counting on Na to replace Cu in some way. Also, we were determined to eliminate trichloro,trifluoro-ethane completely, so we tried two additional procedures with trichloro-ethane. The first was a split soak with methanol having methanol as the initial and trichloro,trifluoro-ethane as the final solvent. The results are shown in figure 2. As can be seen, the results are similar to the previous case but the Voc's on the Cu side are notably lower. In fact the behavior is spotty in that several devices had very low Voc's suggesting shunting. This also seems to coincide with the observance of a white spotty residue on the surface that this combination of solvents could not eliminate. We speculate again that Na is in excess here, and perhaps the areas with white residue contain concentrated Na levels.

In another experiment we tried replacing trichloro-ethane in the above with trichloro-ethylene as the final solvent soak. The results are shown in figure 3. There are both similarities and differences to what was observed above. First, the behavior is again spotty, and as above with methanol/trichloro-ethane, methanol/trichloro-ethylene produces white residue. Putting this aside, however, it appears that the gradient in Voc in going from the In

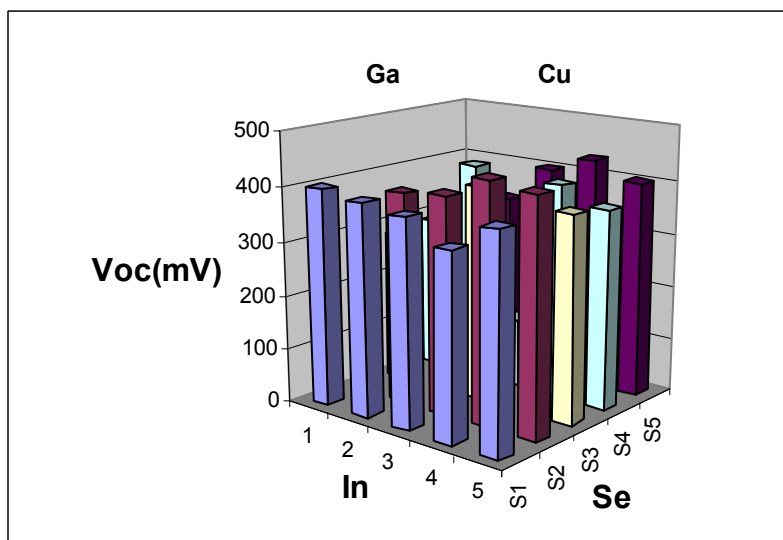


Figure 3. Voc profile of 25 CIGS devices resulting from use of methanol/trichloro-ethylene as the glass cleaning agent.

to the Cu side is not observed here. Nevertheless, Voc is down in the good areas by 50 mV, and Jsc's for all of these solvents were down in the 25 mA/cm² range. The QE spectra were downshifted uniformly which we usually interpret in terms of interface effects. Collectively these results graphically demonstrate how sensitive device performance is to every process detail. And the effects can be manifested in any or all device parameters, and can be bulk or interface driven. Fortuitously, our next solvent candidate, 2-propanol, brought us back on track. The entire ultrasonic soak was done just with 2-propanol as was the case for trichloro,trifluoro-ethane. The Voc profile is shown in figure 4. As can be seen, except for some drop-offs in the corners, the Voc's are clustered in the 450 mV range, and the Jsc's and FF's are up to trichloro,trifluoro-ethane values as well. 2-propanol is relatively inexpensive and user friendly, so it has become our standard solvent. While we have solved our original problem, in the process we uncovered additional layers of materials interactions that must ultimately be understood and controlled. We'll pick this up again at an appropriate time.

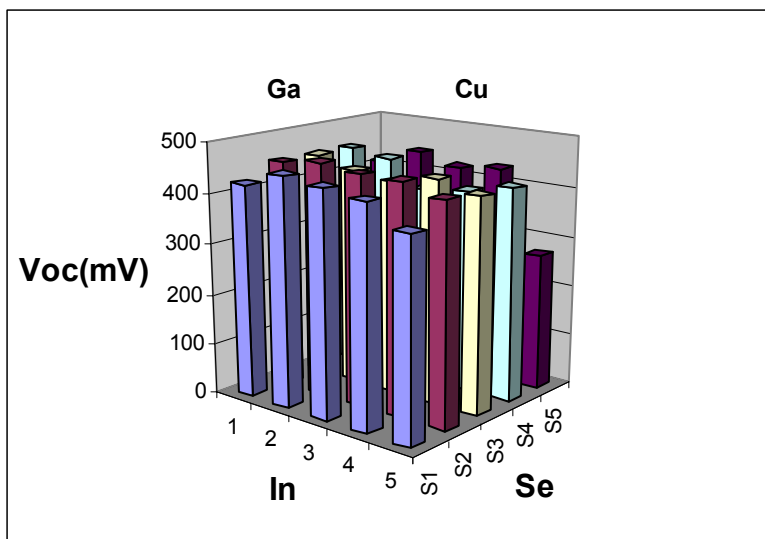


Figure 4. Voc profile of 25 CIGS devices resulting from use of 2-propanol as the glass cleaning agent.

Top Surface Effects – Adjusting the Surface Metal Ratios

In fabricating our standard devices we deposit a final Cu layer thickness of about 25 Å and then complete the selenization step. Typically this final Cu layer is deposited at about 450 ° C. This procedure is at odds with most deposition procedures reported in the literature, but it produces the best results for our process. The effect of the top Cu layer is shown in the data in Table I below.

Sample No.	Top Cu(Å)	Voc(mV)	Isc(mA)
282-01	0	435	3.9
282-03	0	435	4.4
286-01	25	450	3.1
286-03	25	450	4.0

Table I. Effect of top Cu on performance

As can be seen the top Cu layer adds about 15 mV to Voc. The Isc values indicated that to first order Jsc is unaffected. That is, the variation is due to fluctuation in the device areas which nominally are about 0.1 cm². We are not certain why it is necessary to adjust the top metal ratio in this way. It is thought that In₂Se is a volatile species whose formation would be promoted by exposing the growth surface to a low Se flux level. We have tried systematically lowering the final Se flux exposure level to effect removal of In from the top surface which might be expected to reduce or eliminate the need for the top Cu layer. Our results, however, have not supported this expectation. To further enhance the likelihood of forming In₂Se and then having it volatilize

and remove In from the surface we also raised the substrate temperature at the end of the run. The results are shown in Table II.

Sample No.	Temp.(°C)	Voc(mV)	Isc(mA)
272-01	520	385	3.2
272-16	520	395	1.8
277-24	550	435	3.0
277-13	550	425	3.2
278-01	575	440	0.1
278-05	575	445	0.1

Table II. Effect of selenization temperature without top Cu.

For these runs the top Cu was eliminated to see if the desired surface metal ratio could be achieved by removing In rather than adding Cu. As can be seen, the Voc's increased as the temperature was increased which is consistent with expectations. However, at our standard maximum temperature of 550 °C Voc is still about 20 mV lower than the case above with 25 Å of top Cu present. We can continue to further improve Voc by further raising the temperature to 575 ° C, but as can be seen, Isc plummets. The Isc's basically hold steady up to 550 °C. The apparently low value for device 272-16 is due to area and contact fluctuations, and QE spectra indicate that the Jsc's for temperatures at 550 °C and below are comparable. At 575 ° C, however, Isc drops so much that it was difficult to attain a QE spectrum. Since these are surface effects, our experience with simulations suggest that the whole QE spectrum is dropping. Further work will be required to verify this expectation. However, it is clear that the expected removal of In from the surface by volatilization is not achieving the same surface properties as adding the top Cu layer. We expect that the Cu/Group III ratio may be playing a role here in addition to that of Cu/In.

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